ESR STUDY OF THERMAL DEGRADATION OF PVC

By

J. MENCZEL, J. VARGA, K. JUHÁSZ and M. BINETT

Department of Plastics and Rubber, Technical University, Budapest

Received March 13, 1978

Presented by Prof. Dr. Gy. HARDY

It is well known that the reason of relatively low-temperature thermal degradation of PVC is caused by different irregular structures [1], as unsaturated ending groups, unsaturated groups within a chain, the branching of PVC molecules, the head-to-head structures, the oxygen-containing groups, etc.

There are some arguments that this process may follow a radical mechanism. The rate of dehydrochlorination is increasing if the PVC sample contains radical initiators and decreasing in the presence of inhibitors of free radical processes.

Benzene and other hydrocarbons are formed, as a result of PVC degradation [2]. By the ionic and ionic-molecular mechanism the only degradation product may be hydrogen chloride.

However, there is no unambiguous evidence whether the thermal degradation of PVC is a radical or an ionic-molecular process.

OUCHI [4] studied electron spin resonance (ESR) spectra recorded in PVC heat treated above and below 400 °C in air and in vacuum. He suggested that aromatic structures may be formed, as a result of main chain break caused by oxidation and of dehydrochlorination. The stability of ESR-spectra above 400 °C suggested that the unpaired electron may not occupy the conjugated double bond orbital, which may be formed as a result of dehydrochlorination of PVC chains. The presence of aromatic structures in heat-treated PVC was detected by IR spectroscopy [4].

Experimental

In the current work ESR spectra of PVC samples heat-treated at 180 °C, unstabilized (labelled by K-19) and stabilized by 2% of barium stearate (labelled by K-22) and cadmium stearate (labelled by K-25) were studied.

ESR spectra were recorded on a JEOL-type JES-PE-IX ESR-spectrometer using 100 KHz field modulation at 9250 MHz. Spin concentrations were determined using Varian standards; g-factors were calculated from positions of the third and fourth lines of a JEOL Mn^{2+} marker contained in MgO.

All experiments were carried out in air.

Local spin concentrations were calculated from the formula

$$[R^{\cdot}]_{\mathrm{loc}} = \frac{\Delta H_{pp}}{B}, \qquad \text{where}$$

$B = 6.5 \cdot 10^{-20}$ G/cm^3 [3], and ΔH_{pp} — is the peak-to-peak line width, Gauss.

The spin–spin relaxation time was determined from the line width by the formula:

$$T_2 = \frac{1.3131 \cdot 10^{-7}}{g \cdot \Delta H_{pp}}\,.$$

Results and discussion

At room temperature non-heat-treated PVC samples exhibited a singlet ESR spectrum of very weak intensity with $\Delta H_{pp} = 10 - 12$ G. The origin of this line is not clear. Unfortunately, in consequence of the very low intensity of the mentioned line, the line shape may not be exactly determined. However, it is probable that this line is not coming from peroxide radicals, but rather corresponds to polyenyl radicals with the number of conjugation $n \approx 5$.

The temperature of samples was raised in about 5 min to 180 °C in the ESR cavity and the signal was recorded during 6 hours. About 30 min after the experimental temperature was reached, the ESR signal begin to intensify. The average spin concentration for all samples increased with time (Fig. 1). The character of ESR spectra did not change during the heat treatment, in all cases singlet ESR spectra were recorded.

g-factors, spin–spin relaxation times (T_2) and local spin concentrations ($[R]_{loc}$) for PVC samples are shown in Tables 1, 2, and 3.

For the samples K-19 (unstabilized) and K-22 (stabilized by Ba stearate) gradual decrease of the line width was observed, whereas for the sample K-25 (stabilized by Cd stearate) an initial increase of the line width was recorded (Fig. 2). It is possible that this phenomenon is in connection with the formation of a small amount of Cd complexes.

The problem of structure of free radicals formed during the thermal degradation of PVC is not solved yet in the literature.

In our opinion, interpretations published in the literature don't correctly describe the thermal degradation of PVC, but in certain periods of the degradation [4, 5].

From Onishi's interpretation (in his opinion the singlet ESR signal is coming from polyenyl type radicals) a conclusion could be drawn that a singlet with $\Delta H_{pp} = 6$ G could be obtained if the number of conjugated double bonds

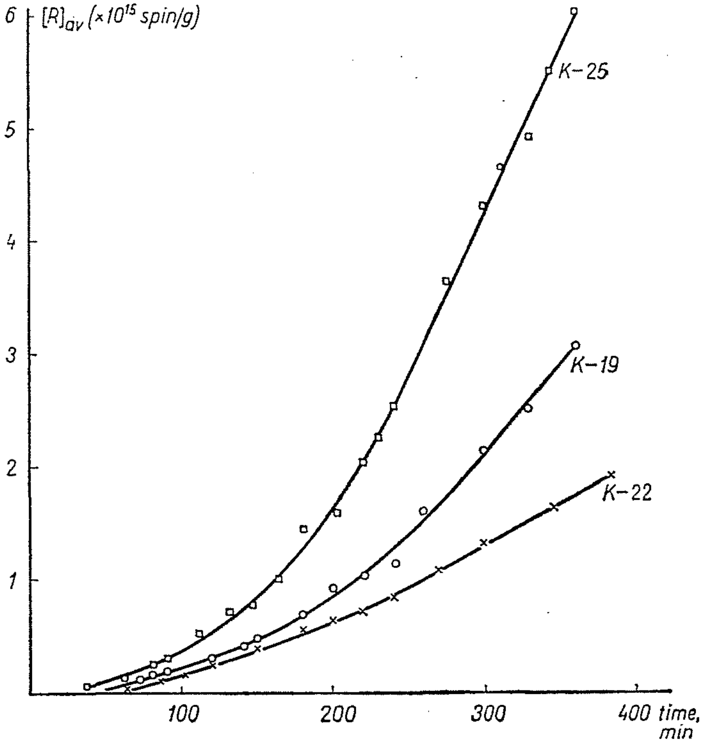

Fig. 1. Dependence of the average radical concentration in PVC samples heat-treated at 180 °C on the heat-treatment time ○ K-19; □ K-25; × K-22

Table 1

Parameters of free radicals formed in the unstabilized PVC sample (K-19) heat treated at 180 °C

Time, min	g-factor	T_2	$[R]_{loc}$
11	2.0036	4.5×10^{-9}	2.24×10^{20}
25	2.0036	7.0×10^{-9}	1.44×10^{20}
50	2.0036	7.5×10^{-9}	1.35×10^{20}
70	2.0036	8.0×10^{-9}	1.26×10^{20}
90	2.0033	8.0×10^{-9}	1.26×10^{20}
100	2.0033	8.0×10^{-9}	1.26×10^{20}
120	2.0033	9.4×10^{-9}	1.08×10^{20}
140	2.0033	10.2×10^{-9}	0.99×10^{20}
180	2.0032	11.2×10^{-9}	0.90×10^{20}
220	2.0032	11.2×10^{-9}	0.90×10^{20}
260	2.0032	11.2×10^{-9}	0.90×10^{20}
320	2.0032	11.2×10^{-9}	0.90×10^{20}
360	2.0032	11.2×10^{-9}	0.90×10^{20}

Table 2

Parameters of free radicals formed in the PVC sample stabilized by 2% of Cd stearate (K-25) heat treated at 180 °C

Time, min	g-factor	T_2	$[R]_{loc}$
10	2.0038	6.7×10^{-9}	1.51×10^{20}
35	2.0038	6.2×10^{-9}	1.64×10^{20}
60	2.0036	5.9×10^{-9}	1.72×10^{20}
80	2.0034	5.9×10^{-9}	1.70×10^{20}
90	2.0034	6.2×10^{-9}	1.64×10^{20}
110	2.0034	6.9×10^{-9}	1.47×10^{20}
130	2.0034	7.5×10^{-9}	1.34×10^{20}
160	2.0034	8.1×10^{-9}	1.25×10^{20}
200	2.0030	9.5×10^{-9}	1.06×10^{20}
230	2.0030	9.5×10^{-9}	1.06×10^{20}
275	2.0030	9.5×10^{-9}	1.06×10^{20}
313	2.0030	9.9×10^{-9}	1.02×10^{20}
360	2.0030	9.9×10^{-9}	1.02×10^{20}

Table 3

Parameters of free radicals formed in the PVC sample stabilized by 2% Ba stearate (K-22) hea treated at 180 °C

Time, min	g-factor	T_2	$[R]_{loc}$
25	2.0061	5.9×10^{-9}	1.72×10^{20}
55	2.0061	7.5×10^{-9}	1.35×10^{20}
63	2.0061	7.6×10^{-9}	1.32×10^{20}
120	2.0061	8.0×10^{-9}	1.26×10^{20}
150	2.0058	8.3×10^{-9}	1.21×10^{20}
180	2.0058	8.6×10^{-9}	1.17×10^{20}
200	2.0058	8.6×10^{-9}	1.17×10^{20}
220	2.0058	9.4×10^{-9}	1.08×10^{20}
240	2.0058	9.4×10^{-9}	1.08×10^{20}
300	2.0058	9.4×10^{-9}	1.08×10^{20}
330	2.0058	11.7×10^{-9}	0.86×10^{20}
345	2.0058	12.5×10^{-9}	0.81×10^{20}
360	2.0058	12.5×10^{-9}	0.81×10^{20}

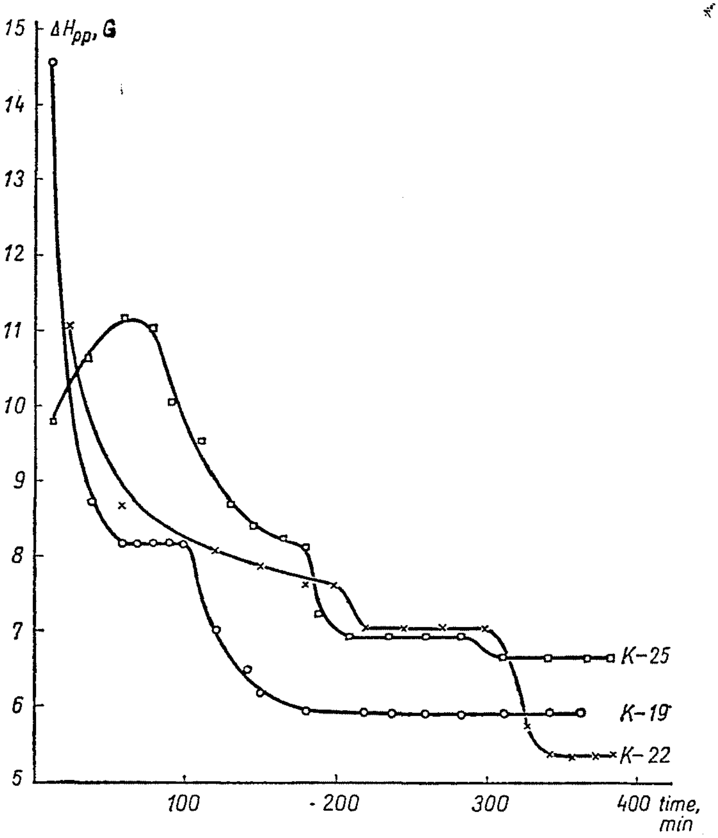

Fig. 2. The peak-to-peak line width (H_{pp}, G) of ESR-spectra of PVC samples heat treated at 180 °C as a function of the heat treatment time ○ K-19; □ K-25; × K-22

(n) much exceeded 20. By this reason we think that Onishi's interpretation is true at the initial period of the degradation.

From the dependence of the line width on the heat treatment time (Fig. 2) it follows that more or less sudden changes in the line width can be observed for all PVC samples. From this fact a conclusion may be drawn that during the heat treatment, changes in the radical structure occur.

On the basis of the line width changes for PVC samples, the following processes are supposed to be accomplished during the thermal degradation:

a. *The PVC sample K-19 (unstabilized)*

In the initial period of thermal degradation polyenyl type radicals containing a number $n = 6$ to 10 of conjugated double bonds are formed. This conclusion may be drawn from the line width $\Delta H_{pp} = 10$ to 15 G. As the heat treatment continues, the line width decreases to $\Delta H_{pp} \approx 8$ G. It seems to be

Table 4

Change of the line shape during the heat treatment of PVC samples (the line shape is presented as combination of Lorentzian and Gaussian line shapes)

Time, min	Lower field part of the line	Higher field part of the line
	Sample K-19	
60	0.4 G + 0.6 L	0.5 G + 0.5 L
90	0.7 G + 0.3 L	0.5 G + 0.5 L
140	0.7 G + 0.3 L	0.5 G + 0.5 L
200	0.8 G + 0.2 L	0.6 G + 0.4 L
220	0.8 G + 0.2 L	0.6 G + 0.4 L
360	0.8 G + 0.2 L	0.6 G + 0.4 L
	Sample K-22	
55	0.5 G + 0.5 L	0.5 G + 0.5 L
150	0.7 G + 0.3 L	0.6 G + 0.4 L
200	0.8 G + 0.2 L	0.7 G + 0.3 L
360	0.8 G + 0.2 L	0.7 G + 0.3 L
	Sample K-25	
35	0.2 G + 0.8 L	0.3 G + 0.7 L
60	0.4 G + 0.6 L	0.3 G + 0.7 L
146	0.5 G + 0.5 L	0.4 G + 0.6 L
205	0.6 G + 0.4 L	0.5 G + 0.5 L
225	0.7 G + 0.3 L	0.6 G + 0.4 L
360	0.8 G + 0.2 L	0.7 G + 0.3 L

probable that this decrease is not a consequence of some change in the radical structure, but rather the exchange effect constrict the signal (a similar effect was observed by Onishi for the heat-treated polyacetylene). After this the line width does not change up to 100 min of the heat treatment time, where a further decrease is observed (from $\Delta H_{pp} = 8$ G to $\Delta H_{pp} = 6$ G). It is supposed that this line thinning is connected with the formation of radicals of different (not polyenyl type) structure. Subsequently, no considerable changes in the line width could be observed, but at about 200 min after the beginning of the heat treatment, there is a slight change in the line shape (Table 4).

Summing up these results it can be supposed that from polyenyl type radicals appearing at the beginning period of the heat treatment, radicals with aromatic structures are formed. This change in the radical structure is accomplished 100 to 180 min after the beginning of the heat treatment. Later no change in the radical structure occurs, but there is an increase in the average spin concentration with time. It may be supposed that radicals are later formed within spin-packets of a constant local concentration ($[R]_{loc} = 1 \times 10^{20}$ spin/g).

b. *Stabilized PVC samples*

From Fig. 2 it is seen that the presence of the stabilizer causes changes in the time dependence of the line width. The presence of the stabilizer undoubtedly has an effect on the structure of radicals formed. This is seen from the fact that three changes for the sample K-25 and two changes for the sample K-22 in the radical structure were observed.

The largest value in local radical concentrations was observed for the sample K-25. In accordance with the time dependence of average radical concentration, this fact supposes that the presence in the sample of Cd stearate promotes the formation of higher radical concentration. At the same time Ba stearate hinders the increase in the radical concentration.

The way of calculating local concentration values refers to the Lorentzian line shape. However, the difference between the local concentrations is much greater than the value of the relative error (to a degree that the ESR signals in the final period of the heat treatment have the same line shape for any sample, see Table 4).

The average radical concentrations are plotted as a function of hydrogen chloride split off to the corresponding time (Figs 3, 4, 5).

From these figures the average spin concentration is seen to be in certain correlation with the dehydrochlorination of PVC samples.

For the samples unstabilized (K-19) and containing Ba stearate (K-22) an approximate linear correlation may be observed, but for the sample containing Cd stearate (K-25) a slightly ascending curve is obtained.

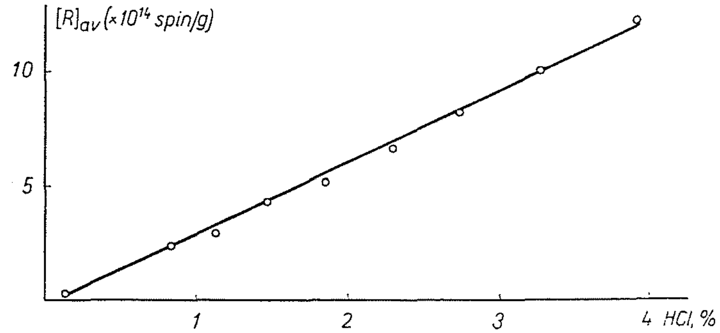

Fig. 3. The average radical concentration as a function of dehydrochlorination of the unstabilized PVC sample

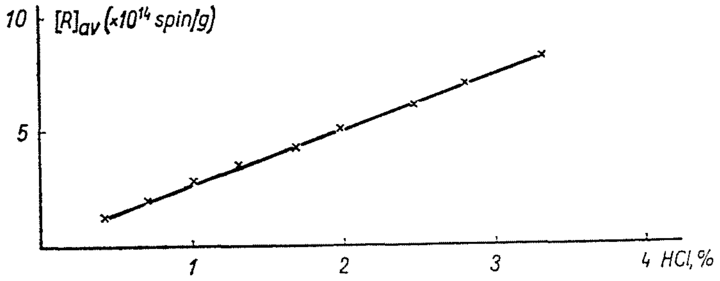

Fig. 4. The average radical concentration as a function of dehydrochlorination of the PVC sample stabilized by 2% Ba stearate

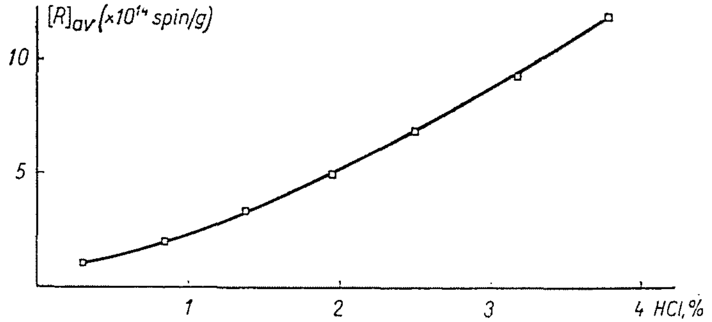

Fig. 5. The average radical concentration as a function of dehydrochlorination of the PVC sample stabilized by 2% Cd stearate

Summary

In the current work free radicals formed in the course of thermal degradation of PVC have been studied by ESR spectroscopy. The changes in line width and line shape were studied using pure PVC sample, as well as PVC samples containing 2% of Ba stearate or Cd stearate as stabilizers. It has been established that radicals of different structures are formed in different periods of thermal degradation. Approximately linear correlation is observed between the average radical concentration and the dehydrochlorination of PVC.

References

1. Baum, B.—Wartman, L. H.: J. Polym. Sci., **28**, 537 (1958)
2. Moiseev, V. D.—Suskina, V. I.—Neiman, M. B.: Plastmassy, N2, (1966)
3. Chachaty, C.—Forchioni, A.: J. Polym. Sci., **10**, 129 (1972)
4. Ouchi, J.: J. Polym. Sci., **A3**, 2685 (1965)
5. Onishi, S.—Nakajuma, Y.: J. Appl. Polym. Sci., **6**, 629 (1962)

Dr. József Menczel
Dr. József Varga
Dr. Kálmán Juhász
Mariann Binett
H-1521 Budapest